

Glass fiber catalysts for total oxidation of CO and hydrocarbons in waste gases

L. Kiwi-Minsker^a, I. Yuranov^a, B. Siebenhaar^b, A. Renken^{a,*}

^a *Institute of Chemical Engineering, EPFL, Lausanne, Switzerland*

^b *Novartis Services AG, Switzerland*

Abstract

Different glass fibers in woven forms were used as supports for Pt and Pd catalysts and were tested in toluene and CO total oxidation at atmospheric pressure. The catalytic activity and the ignition-extinction temperatures were investigated in relation to chemical composition of the supports, the types of active metal used (Pt, Pd), and the surface concentration of the metal. The experimental results suggest the modified glass fibers as suitable supports for efficient catalysts for complete oxidation. The catalysts can be used at moderate temperatures (150–250°C) and at high gas hourly space velocity (GHSV = 30 000 h⁻¹). The main design parameters of structured catalytic bed reactors, based on glass fiber catalyst, are discussed. ©1999 Elsevier Science B.V. All rights reserved.

Keywords: Glass fibers; Oxidation; CO; Hydrocarbons; Waste gases

1. Introduction

The problem of air pollution abatement from exhaust gases is a topic of growing concern in relation to the complete oxidation of volatile organic compounds (VOCs) and carbon monoxide. The main processes currently used are thermal and catalytic incinerations. In both processes the organic compounds are completely oxidized by oxygen to carbon dioxide and water. Incineration processes are predominantly used for large gas flows containing varying concentrations of VOCs in the range of 0.5–10 g m⁻³ (STP). Whilst thermal incinerators have proved to be reliable at large scale operation, they show important drawbacks. The disadvantages are mainly the high fuel consumption

and formation of toxic compound like NO_x and dioxines due to the high operating temperature employed.

The incinerators based on catalytic combustion do not have the above mentioned drawbacks. Due to much lower operating temperatures, the formation of toxic compounds can generally be avoided. Gas temperatures are typically below 400°C. The gas hourly space velocity (GHSV) required is in the range of 1000–100 000 h⁻¹. For economical reason the pressure drop in the catalytic converter should be as low as possible. Therefore, highly active catalysts are desirable in order to get complete oxidation at short residence time. The catalysts used for combustion are mainly noble metals supported on a variety of materials, such as pellets, honeycomb monolith, parallel plates, fiber pads, and gauze or sintered metals.

Current development on combustion catalyst aims at improving the catalytic activity. This development

* Corresponding author. Tel.: +41-21-693-31-81; fax: +41-21-693-31-90

E-mail address: albert.renken@epfl.ch (A. Renken)

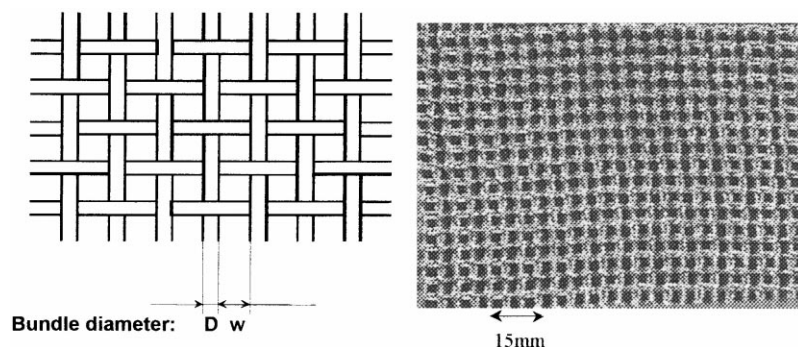


Fig. 1. Schematic presentation and real view of one glass fiber catalytic layer.

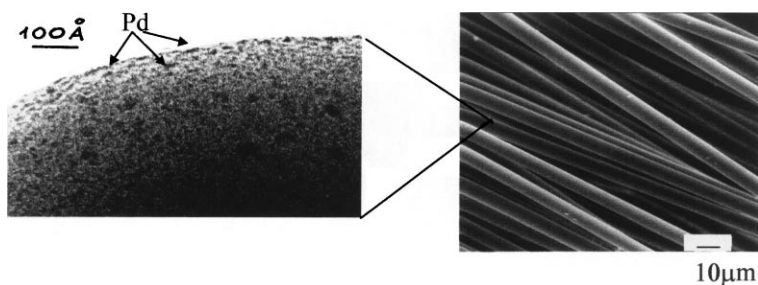


Fig. 2. Electronic microscopy view of elementary glass filaments and Pd supported on their surface.

involves finding better support materials for the active component, providing easy gas passage with concomitantly low-pressure drop in the reactor. The honeycomb ceramic monoliths have been suggested as one of valuable designs for the catalytic bed in combustion reactors. This reactor offers several advantages in comparison with conventional randomly packed-beds [1]. They have an open macro-structure, allowing high flow rates through the catalytic beds with low pressure drop and they possess an improved mass transfer properties due to the shortening of the gas diffusion distance. The main drawbacks of monolith reactors are their high manufacturing cost and their susceptibility to thermal and mechanical stresses. Moreover, the optimum performance of the monolith reactor requires uniform and stable distribution of gas over the reactor cross section, which is sometimes difficult to obtain. Therefore, combustion reactor with structured catalytic beds made from glass fiber materials, as suggested hereby, is an alternative solution for the problems encountered in other types of reactors.

The glass fiber (GF) support is woven from long threads consisting of a bundle of elementary filaments. The diameter of one filament ranges from 3 to 15 mm. Glass fiber materials in woven form can be designed with a variety of macro-structures, such as tissue, gauze (see Fig. 1) or 3D-blocks. It offers a large spectrum of options in the reactor design with structured catalytic beds.

The GF catalyst is made by the deposition of different active metal ions on the amorphous glass matrix. The electron microscopic images of glass filaments and of supported Pd on filament surface are presented in Fig. 2.

Supported noble metal catalysts deposited on glass fiber have already shown promises for the catalytic converter technology [2–4]. Recently, we reported the results [4] on the catalytic ignition-extinction limits and on the oscillatory behavior of CO oxidation reaction. The influence of catalyst microstructure, specific surface area, surface concentration and dispersion of the active component on the catalyst efficiency were investigated.

Table 1
Characteristics of the glass fiber supported catalysts used for CO oxidation

Number	Catalyst	Metal content (wt.%)	SSA (m ² g ⁻¹)	Metal surface concentration (mmol m ⁻²)	<i>R</i> (180°C) (mol _{CO} g _{Pd} ⁻¹ s)	<i>R</i> (180°C) (mol _{CO} g _{cat} ⁻¹ s)	<i>T</i> _{ig} °C (1%CO)
1	0.002 Pd/SGF-2	0.002	2	1.0 × 10 ⁻⁴	–	–	255
2	0.02 Pd/SGF-2 ^a	0.02	2	1.0 × 10 ⁻³	1.1 × 10 ⁻⁴	2.2 × 10 ⁻⁸	230
3	0.2 Pd/SGF-2 ^a	0.2	2	1.0 × 10 ⁻²	2.4 × 10 ⁻⁵	4.8 × 10 ⁻⁸	225
4	0.2 Pd/EGF-2 ^b	0.2	2	1.0 × 10 ⁻²	1.3 × 10 ⁻⁴	2.6 × 10 ⁻⁷	185
5	0.2 Pd/EGF-15 ^a	0.2	15	1.3 × 10 ⁻³	2.0 × 10 ⁻⁴	4.0 × 10 ⁻⁷	165
6	0.2 Pd/EGF-70 ^a	0.2	70	2.7 × 10 ⁻⁴	6.6 × 10 ⁻⁵	1.1 × 10 ⁻⁷	220
7	1.0 Pd/EGF-70 ^a	1.0	70	1.3 × 10 ⁻³	2.5 × 10 ⁻⁴	2.5 × 10 ⁻⁶	155
8	0.02 Pt/SGF-2 ^a	0.02	2	1.0 × 10 ⁻³	6.6 × 10 ⁻⁵	1.1 × 10 ⁻⁸	230
9	0.2 Pt/EGF-15 ^a	0.2	15	1.3 × 10 ⁻³	9.2 × 10 ⁻⁵	1.8 × 10 ⁻⁷	195

^a The content of active metal corresponds to ion-exchange capacity of the support.

^b The catalysts were prepared by impregnation method.

The purpose of present study is to further develop the GF based catalysts for their application in the combustion reactor design with structured catalytic beds for VOCs and CO abatement. Complete oxidation of carbon monoxide and toluene were chosen as compounds to simulate exhaust gases produced from stationary sources. The study will evaluate the catalyst activity and ignition-extinction limits as a function of chemical composition of the support and noble metal loading.

2. Experimental

2.1. Catalyst preparation and characterization

Two types of commercial glass fibers produced by 'Steklovolokno' (Polotsk, Belarus) were used as starting materials for the preparation of the GF supports: silica glass fibers (SGF) and alumoborosilicate glass (E-type) fibers (EGF). The specific surface area (SSA) of the starting glass fiber materials is 2 m² g⁻¹, which corresponds approximately to the geometrical specific surface of the filaments. The samples of EGF in woven form were pre-treated in aqueous solutions of HCl in order to develop porosity and to increase the SSA. The strong acid attacks the EGF surface leaching out the vol %-silica components. The samples were then rinsed in distilled water and dried at 50°C. The SSA of the supports was varied between 2 and 275 m² g⁻¹ by variation of pre-treatment conditions employed, i.e., temperature and time of contact with the acidic media.

In some cases, the surface of fibrous supports was modified by titania (TGF) and zirconia (ZGF) in order to study the effect of the support composition on the catalytic properties of the material obtained.

Palladium (II) chloride (PdCl₂) and chloroplatinic acid (H₂PtCl₆) (purum, Fluka Chemie AG, Buchs, Switzerland) were used as precursors of the active components. The Pd and Pt supported GF catalysts were prepared by the metal deposition from aqueous NH₃ solutions via well-known ion-exchange method [3], or by wet-impregnation, followed by calcination at 450°C on air during 3 h. The content of Pd and Pt was varied from 0.02 to 1.0 wt.%. Before the reaction the catalysts were reduced in flow of hydrogen (3% in Ar) at 300°C for 3 h. The main characteristics of the catalysts are presented in Tables 1 and 2.

The BET surface area (SSA) and pores size distribution of the supports and catalysts were measured using N₂ adsorption-desorption at 77.3 K via a Sorptomatic 1990 (Carlo Erba) apparatus. Active sites were determined by CO chemisorption. The total amount of metal was measured by atomic absorption spectroscopy.

2.2. Experimental set-up

The experimental set-up for the study of CO oxidation is presented in Fig. 3. The reactor used was a continuous fixed bed reactor with an external recycle loop and a membrane compressor. The recycling ratio in the system was never less than 100. Therefore,

Table 2

Characteristics of the GF catalysts used for toluene oxidation

Number	Catalyst	Metal content (wt.%)	SSA ($\text{m}^2 \text{g}^{-1}$)	Metal surface concentration (mmol m^{-2})	T_{ig} ($^{\circ}\text{C}$)	T_{ext} ($^{\circ}\text{C}$)
1.	0.2 Pd/EGF-15	0.2	15	1.3×10^{-3}	265	200
2.	0.2 Pd/TGF-56	0.2	56	3.5×10^{-4}	260	145
3.	0.2 Pd/ZGF-160	0.2	160	1.2×10^{-4}	255	100
4.	0.2 Pt/EGF-15	0.2	15	1.3×10^{-3}	250	<60
5.	0.2 Pt/TGF-56	0.2	56	3.5×10^{-4}	230	72

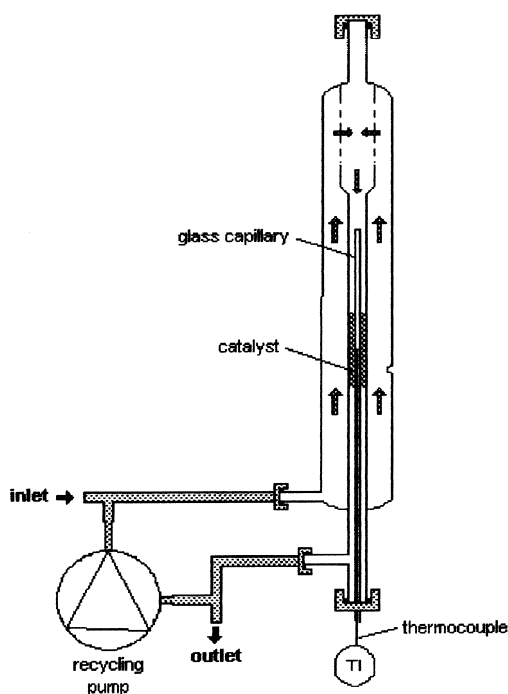


Fig. 3. Recycle reactor for CO oxidation.

the reactor could be considered as an ideal continuous stirred tank reactor (CSTR) [5].

Rolled up woven GF catalyst (mass about 0.4 g) was placed into the middle part of the reactor. The temperature in the catalytic bed was measured by a sheathed thermocouple.

The gases CO, CO₂, O₂, and Ar (99.9%, Carba-Gas, Lausanne, Switzerland) were used without further purification. The total gas feed rate was 6–12 l h⁻¹ and was supplied through mass flow controller. The CO concentration in the feed was varied from 0.1 to 2.5 vol %, the O₂ concentration was always kept at 10 vol % and argon was used as diluent gas. Outlet CO

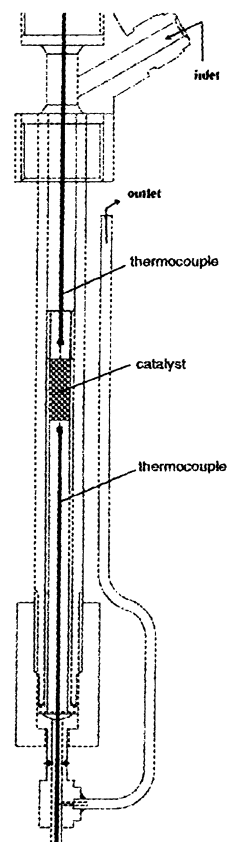


Fig. 4. Tubular reactor for toluene oxidation.

and CO₂ concentrations were continuously monitored by an infrared analyzer Ultramat 22P (Siemens).

The reaction rate R was calculated as the amount of CO moles reacted per second per gram of Pd and was used as a characteristic of catalytic activity.

The toluene oxidation was carried out in a stainless steel fixed-bed plug-flow micro-reactor (Fig. 4). The concentration of toluene (purum, Fluka Chemie AG, Buchs, Switzerland) in air was in the range

of 0.3–2.4 vol %. The flow rate of toluene was 0.9–5.0 mmol h⁻¹, air flow rate was 6 l h⁻¹. The catalyst (about 0.2 g) was placed into the middle part of the reactor. The inlet gas-mixture was pre-heated and the temperature of inlet and outlet gas was registered by two thermocouples placed before and after catalytic bed. The thermocouples can be positioned with a precision of 1 mm. Errors in the temperature measurements lie in the order of $\pm 0.5^\circ\text{C}$. The concentrations of outlet gases were monitored by mass spectroscopy. The temperatures of ignition (T_{ig}) and extinction (T_{ex}) were measured at the catalytic bed inlet and used for comparison of catalytic activity.

3. Results and discussion

3.1. CO oxidation

The oxidation of CO over noble metal containing demonstrates nonlinear kinetics resulting in observed temperature/concentration hysteresis, steady-state multiplicity and long-lasting self-sustained isothermal oscillations [6–10].

All GF catalysts studied in CO oxidation demonstrate the temperature hysteresis as shown on Fig. 5. The reaction rate increases slowly with increasing temperature up to the ignition temperature (T_{ig}), where the jump into the ignited state (high reactivity regime) is observed. Above the T_{ig} , conversion of CO was close

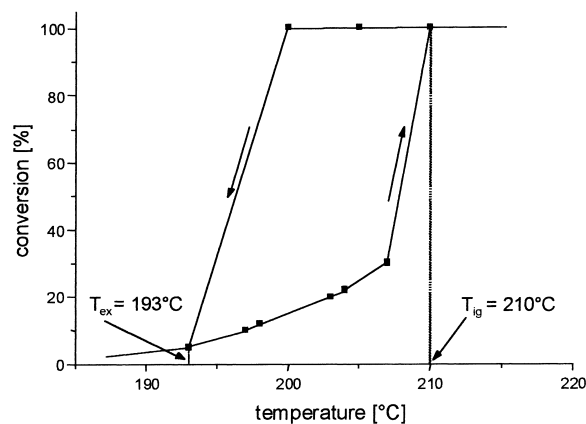


Fig. 5. Temperature hysteresis for CO oxidation over 0.02Pd/SGF-2 ($m_{\text{cat}} = 0.8 \text{ g}$; $C_{\text{CO}} = 1 \text{ vol \%}$; $C_{\text{O}_2} = 10 \text{ vol \%}$; $Q = 12 \text{ l h}^{-1}$ (STP)).

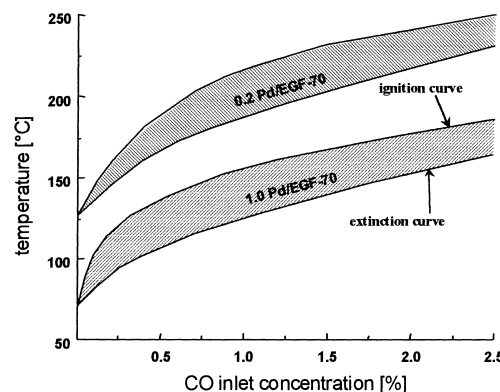


Fig. 6. Dependence of ignition and extinction temperatures on CO concentration ($m_{\text{cat}} = 0.4 \text{ g}$; $C_{\text{O}_2} = 10 \text{ vol \%}$; $Q = 6 \text{ l h}^{-1}$ (STP)).

to 100% for all catalysts studied. If the temperature in the catalytic bed is decreased, high CO conversion remains until the temperature of extinction (T_{ex}) is reached. At T_{ex} the reaction enters the low reactivity regime (extinguished state). In between T_{ig} and T_{ex} the bi-stability region is attained. Within this region the catalyst can be in low or high reactivity states under the same reaction conditions.

Temperatures of ignition and extinction (T_{ig} and T_{ex}) depend on the inlet CO concentration, the gas flow rate and the ramp of the temperature change. The temperature-concentration dependencies at constant gas flow rate and the temperature ramp for two catalysts studied are presented in Fig. 6. The effect of the temperature ramp depend on the dynamics of the system. The temperature ramp was kept constant to get comparable results.

The region formed by the upper curve of ignition and the lower curve of extinction represents the bi-stability region (shaded area). The region of low activity (extinguished state) is under the curve of extinction. The region of the high catalytic activity (ignited state) is above the ignition curve. The extinguished state is characterized by comparatively low conversion (<40%). In the ignited state CO conversion close to 100% is always observed even for a small catalyst loading and a Pd concentration of only 0.002 wt. %.

Under the same operating conditions the values of T_{ig} and T_{ex} are useful to compare activities of different catalysts. For example, from the Table 1 it is

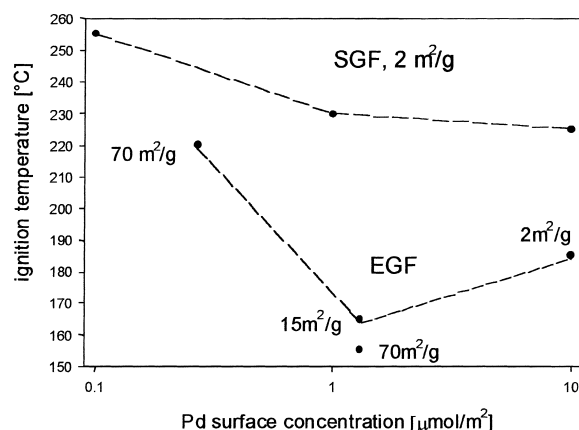


Fig. 7. Dependence of the ignition temperature in CO oxidation on the Pd surface concentration over different glass fiber catalysts.

seen that the T_{ig} depends on the Pd surface concentration and the type of the support used. Thus, for the same support type (SGF) the T_{ig} was observed to decrease when surface Pd concentration was increased from 0.1 to 1.0 mmol m^{-2} and then the T_{ig} remains almost unchanged up to the surface Pd concentration of 10 mmol m^{-2} . The T_{ig} dependence from the surface Pd concentration is presented on the Fig. 7. When the same EGF type of support was used, a more complicated dependence of the reaction rate and T_{ig} on the Pd surface concentration was observed. The T_{ig} first decreases with increase in the surface Pd concentration and then goes up. This behavior can be explained by the variation of the ion exchange capacity of the support due to the acidic treatment. For all supports treated in acidic media in order to increase the SSA the specific ion exchange capacity was found to be about $1.3 \mu\text{mol m}^{-2}$, whereas for nontreated supports the value was much less.

The influence of the support composition on catalytic activity is seen by comparison of the catalyst 3 with the catalyst 4 (see Table 1 and Fig. 7). These two catalysts were identical in Pd surface concentration, SSA ($2 \text{ m}^2 \text{ g}^{-1}$) and the total Pd loading. Only the chemical composition of the fiber support used (silica glass and alumoborosilicate glass) was different. The Pd supported on the SGF demonstrated lower activity (reaction rate more than 5 times smaller) and higher T_{ig} with respect to Pd supported on EGF. The observed lower activity may be explained by strong

interaction of Pd with silica glass support under reaction conditions.

3.2. Toluene oxidation

VOCs removals are usually carried out at low reactant concentrations (often less than 1000 ppm) in industrial processes with large excesses of oxygen (normally in air). Since the concentrations are low, the heat of reaction produced may not be sufficient for self-sustained oxidation. Therefore, the entire gas stream must be heated to elevated temperatures ($>400^\circ\text{C}$) to attain full conversion. For economical catalytic oxidation of trace concentrations of VOCs nonselective and highly active catalysts at low temperatures are required. The requirement of 100% conversion must be taken into consideration since, if the oxidation is not complete, compounds more toxic than VOCs traces may be formed.

The screening of different GF catalysts was carried out for complete toluene oxidation, which was chosen as a model reaction for VOCs removal from industrial exhaust. The catalysts tested demonstrated unstable behavior, which is typical for exothermic reactions with transport limitations [11]. One of the experimental temperature hysteresis observed is presented on Fig. 8. As seen from the figure, no toluene conversion was observed with increase in the inlet temperature up

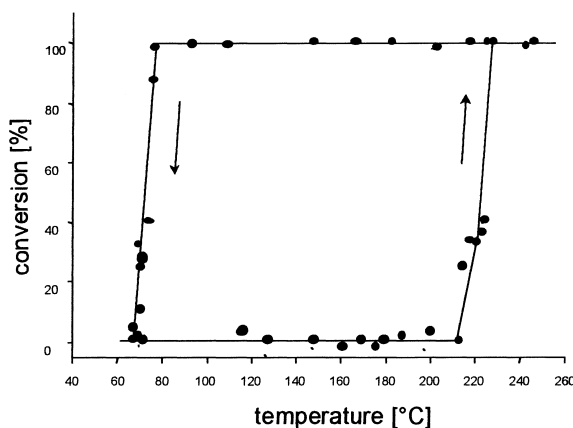


Fig. 8. Temperature hysteresis for toluene oxidation over 0.2Pt/TGF-56 ($m_{\text{cat}} = 0.8 \text{ g}$; toluene feed: 4.7 mmol h^{-1} $Q_{\text{air}} = 61 \text{ h}^{-1}$ (STP)).

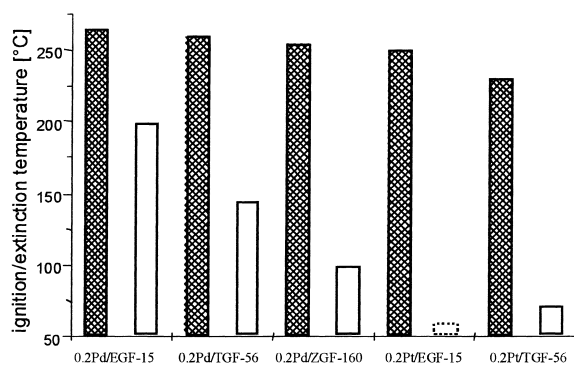


Fig. 9. Ignition and extinction temperatures for toluene oxidation over different glass fiber catalysts.

to a sharp jump-up in the conversion close to 100%. This temperature value was taken as T_{ig} . If the temperature in the catalytic bed inlet was decreased, the toluene conversion of 100% remains until the temperature of extinction (T_{ex}) is reached. At this temperature the reaction rate sharply decreases and no conversion was observed. The temperatures T_{ig} and T_{ex} depend on the inlet concentration of toluene, the gas flow rate and the ramp of the temperature change. Under the same operating conditions the values of T_{ig} and T_{ex} are useful to compare activities of different catalysts. For example, from Fig. 9 and Table 2 both T_{ig} and T_{ex} depend on the noble metal (Pd or Pt) and the type of the support used. The 0.2Pt/EGF-15 catalyst demonstrated the highest catalytic activity as T_{ex} was observed to be lower than 60°C.

The catalytic oxidation reactions used for exhaust abatement from chemical plants have an additional

distinction related to the complex chemical composition of the oxidizing gas-mixture. The gas consists of primarily hydrocarbons and some NH_3 and SO_2 . However, the trace contaminants can frequently include halocarbon solvents, phosphorous- and nitrogen-containing compounds. These contaminants poison conventional industrial oxidation catalysts. Therefore, in this study we test for a poisoning of the catalyst 0.2Pd/EGF-15 by introducing CH_2Cl_2 instead of toluene into the feed. After 1 h treatment the catalyst was again tested for toluene oxidation. Although the starting activity was much lower than the fresh catalyst, the deactivation was observed to be reversible and the catalyst recovered completely its activity after several hours on stream.

3.3. Main characteristics of GF catalytic bed

The use of glass fiber pads and gauze as catalyst supports for catalytic combustors has been known in the field [2,3,12,13]. The porosity of the pads is usually high (up to 90%), which offers a large internal area, but a small pore size. Therefore, these materials are suitable for catalytic supports only in situations where the gaseous feed does not contain particulates. The glass fibers supports in woven form (tissue or gauze) do not have this drawback since micro- and macro-porosity can be regulated on different levels beginning from a single filament, then a bundle, a catalyst layer, and a whole catalytic bed.

The main design parameters of the glass fiber catalytic bed are presented in Fig. 10. The threads of the fabrics consist of 50–100 filaments with a diameter d

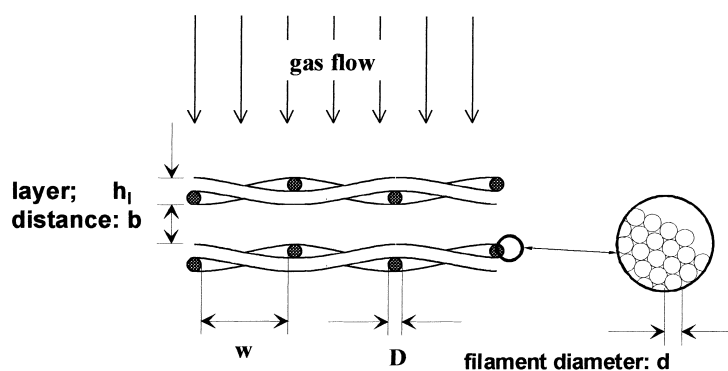


Fig. 10. Scheme of the glass fiber structure.

of 3–15 mm twisted in bundles with a diameter D of several hundred microns. The equivalent diameter of the macro-pores inside the thread is defined by the diameter of the elementary filaments and is in the order of several microns. The characteristic diffusion time in gases is about $t_D = 10^{-6}$ s. Therefore, the transport limitations inside the bundles will not take place for reactions with characteristic reaction times more than 10^{-6} s.

Among the most important characteristics of the structured catalytic packed bed is the pressure drop. The values of this parameter depend on the overall void fraction of the bed (ε_{bed}) defined as the volume of the gas phase referred to the total volume of the reactor and the thickness of one layer (h_l). Besides of the diameter of the threads (D) the ε_{bed} value depends on the width (w) between the threads and the distance between the layers (b). These design parameters can be varied and optimized for the specific reaction conditions.

4. Conclusions

Pd and Pt supported on glass fibers are shown to be active catalysts for the total oxidation of toluene and CO at atmospheric pressure. The catalytic activity depends strongly on the chemical composition of the glass fiber, its specific surface area and metal (Pd, Pt) surface concentration.

The catalyst can be used as effective materials for catalytic incinerators at moderate temperatures (100–250°C) and high Gas Hourly Space Velocities of up to $30\,000\text{ h}^{-1}$. Glass fiber catalysts can be designed in a variety of macro structures offering

a large spectrum of options for the reactor design optimization.

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